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Surface Modification of Titanium-Based Alloy with Ti/C Compositionally Graded Film Deposited by Sputtering

Tsutomu Sonoda, Akira Watazu, Kiyotaka Katou, Takahiko Yamada and Tadashi Asahina
National Institute of Advanced Industrial Science and Technology(AIST)
2266-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya
Fax: 81-52-736-7400, e-mail: tsutomu.sonoda@aist.go.jp

Surface modification of superplastic titanium-based alloy such as Ti-6Al-4V or Ti-4.5Al-3V-2Fe-2Mo with Ti/C compositionally graded film was examined by magnetron sputtering, in order to improve not only the biocompatibility and the abrasion resistance of the alloy but also the adhesion between the deposited film and the alloy substrate with preserving the high hardness of such ceramic coatings. The Ti/C compositionally gradient films were deposited by co-sputtering of two sputter cathodes which had pure titanium and titanium carbide targets respectively, and their compositional gradient was realized by varying continuously the electric power supplied to each sputter cathode. Under visual observation, the obtained film appeared to be uniformed and adhesive. According to AES in-depth profiles, the carbon (C) concentration in the film gradually decreased in depth direction from the surface toward the substrate, confirming that Ti/C compositionally gradient film had formed on the alloy substrate. On the basis of XRD, it was found that titanium carbide (TiC) and α-titanium phases were formed in the films. Furthermore the Vickers hardness of the films reached over Hv1800. Thus both the surface hardness and the adhesion of the deposited hard coatings were expected to be improved at the same time.
Key words: graded coating, sputter-deposition, co-sputtering, titanium carbide, titanium alloy

1. INTRODUCTION

Ti-6Al-4V alloy attracting attention as a biomaterial features excellent mechanical properties and corrosion resistance. However, this alloy contains aluminum and vanadium liable to do serious harm to human bodies [1,2], so actual use will require prevention of direct contact with biological tissues [3-5]. On the other hand, the alloy has poor abrasion resistance to be applied to an artificial joint, so its application will require some surface modification of the alloy such as coating with hard ceramic films. However such hard ceramic coatings might have poor adhesion to the alloy, so it is necessary to form some interlayer between the hard coating and the alloy to relax the stress concentrated at the interface.

Therefore we examined coating of the alloy substrate with Ti/C compositionally gradient film by magnetron DC sputtering, aiming at the application of the alloy to an artificial joint. Because it is expected that coating with the gradient film will improve not only the biocompatibility as a barrier layer preventing such harmful substances from leaching out and the abrasion resistance of the alloy but also the adhesion between the deposited film and the alloy substrate with preserving the high hardness of such a ceramic coating as titanium carbide (TiC) coating [6-9].

2. EXPERIMENTAL

A planar magnetron sputtering system (ANELVA Corp. type L-332S-FHS) with 3 cathodes was used. The planar targets used for this study were a pure titanium disk and a titanium carbide disk of 80 mm-diameter, respectively. Ti-4.5Al-3V-2Fe-2Mo alloy substrates (14×14 mm^2, thickness 0.55 mm) were mounted on the water-cooled substrate holder. The deposition of Ti/C compositionally gradient films was carried out in the atmosphere of argon by co-sputtering of 2 sputter cathodes which had the pure titanium target and the titanium carbide target respectively. The schematic illustration of this co-sputtering is shown in Fig. 1. Their compositionally gradient was realized by varying continuously the electric power supplied to each sputter cathode. The sputtering conditions examined in this study were as follows. The electric power sources supplying to the 2 sputter cathodes with the pure titanium target and the titanium carbide target were of DC (direct current) and of RF (radio frequency), respectively. To realize the Ti/C compositionally gradient in depth direction, the DC power for sputtering the pure titanium target was continuously decreased from 300 W to 0 W with depositing time, while the RF power for sputtering the titanium carbide target was continuously increased from 0 W to 600 W with depositing time. Schematic change in DC electric power supplied for sputtering the pure titanium target and RF power supplied for sputtering the titanium carbide target with depositing time is shown in Fig. 2.

The thickness of deposited films was measured by tracing the substrate-film step using a surface roughness tester [10]. In-depth profiles of the obtained films were analysed by Auger electron spectroscopy (AES) (JEOL Corp. Type JUMP10-SX) with an ion sputter etching method using argon ion beam. Characterization of the films was accomplished by X-ray diffractometry (XRD) (RIGAKU Corp. Type RAD-1B). Hardness was measured using a Vickers hardness tester under 10 g load.

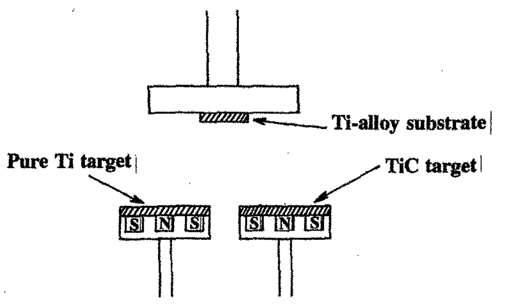


Fig. 1. Schematic illustration of the co-sputtering for the depositon of Ti/C compositionally gradient film onto Ti-alloy substrate.

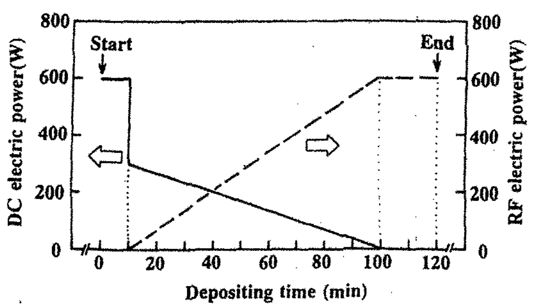


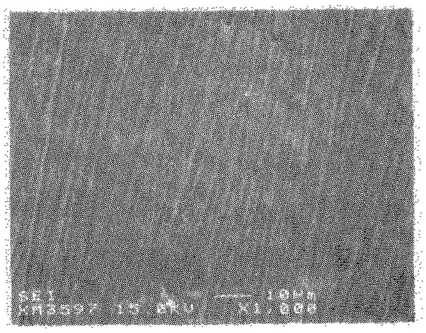
Fig. 2. Schematic change in DC electric power supplied for sputtering the pure titanium target and RF power supplied for sputtering the titanium carbide target with depositing time.

3. RESULTS AND DISCUSSION

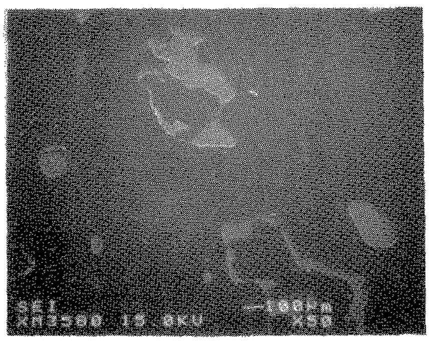
Under visual observation, the obtained Ti/C compositionally gradient film appeared to be uniform and adhesive and their thickness were approximately 3 μm. In contrast, TiC monolithic films deposited onto the Ti alloy by sputtering only the titanium carbide (TiC) target peeled off partly. Figure 3 shows SEM images for the surface of that compositionally gradient film and of the monolithic film.

AES in-depth profiles of Ti, C, Al and O are shown in Fig. 4. According to these in-depth profiles, the carbon (C) concentration in the film gradually decreased in depth direction from the surface toward the substrate, following its constant concentration in depth direction at the range of depth closer to the surface in the film.

This shows that the pattern of the change in carbon (C) concentration along the depth direction was consistent with the model of the change in both electric powers supplied to the pure titanium (Ti) target and the titanium carbide (TiC) target, offered in Fig. 2. Therefore it was confirmed that a Ti/C compositionally gradient film had formed on the alloy substrate. On the other hand, specific increases of the concentration of carbon (C) and oxygen (O) were respectively detected in the vicinity of the interface between the gradient film and the alloy substrate. It is assumed that the carbon atoms and oxygen ones which had existed at the surface of the alloy substrate diffused into the titanium layer of the Ti/C compositionally gradient film.



(a) Ti/C compositionally gradient film



(b) TiC monolithic film

Fig. 3. SEM micrographs for the surface of the Ti/C compositionally gradient film obtained in this study (a) and of the TiC monolithic film deposited onto the Ti alloy by sputtering only the titanium carbide (TiC) target (b).

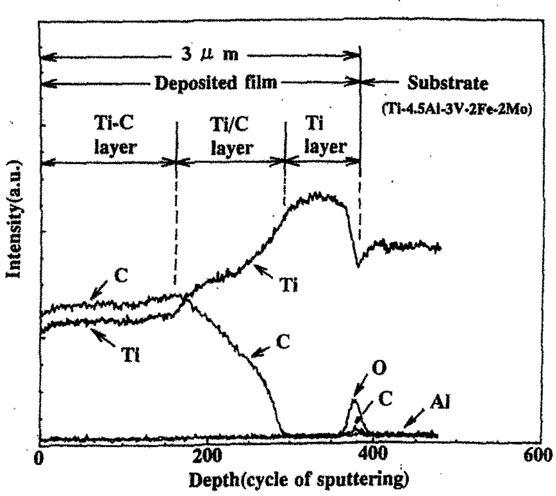


Fig. 4. AES in-depth profiles of Ti, C, Al and O for the deposited film and the Ti-4.5Al-3V-2Fe-2Mo alloy substrate.

Figure 5 shows the X-ray diffraction (XRD) pattern of the deposited Ti/C compositionally gradient film. On the basis of XRD, it was found that titanium carbide and α-titanium phases were formed in the Ti/C compositionally gradient film, with TiC (200) and Ti (010) dominant respectively.

The Vickers hardness of the deposited Ti/C compositionally gradient film, compared with that of the Ti-4.5Al-3V-2Fe-2Mo alloy substrate, is shown in Fig.6. The hardness of the Ti/C compositionally graded film reached Hv=1800, while that of the Ti-4.5Al-3V-2Fe-2Mo alloy substrate approximately indicated Hv=400. Therefore it was found that the hardness of the titanium alloy was considerably improved by coating with the Ti/C compositionally gradient film. Hence the surface hardness resistance of the alloy and the adhesion of the hard coatings were expected to be improved at the same time by this method.

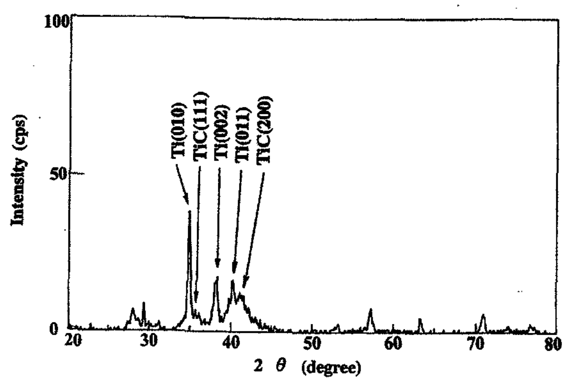


Fig. 5. X-ray diffraction pattern of the Ti/C compositionally graded film deposited onto the superplastic Ti-alloy substrate.

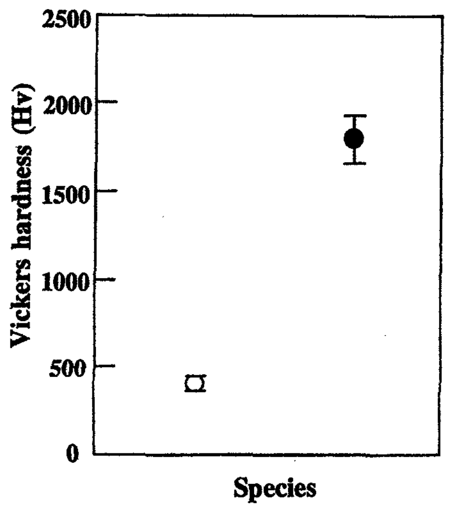


Fig. 6. Vickers hardness of the titanium-based alloy[Ti-4.5Al-3V-2Fe-2Mo](○) and the deposited Ti/C compositionally graded film(●).

4. CONCLUSIONS

Surface modification of superplastic titanium-based alloy such as Ti-6Al-4V or Ti-4.5Al-3V-2Fe-2Mo with Ti/C compositionally graded films was examined by magnetron sputtering, in order to improve not only the biocompatibility and the abrasion resistance of the alloy but also the adhesion between the deposited film and the alloy substrate with preserving the high hardness of such ceramic coatings. The Ti/C compositionally graded film was deposited by co-sputtering of 2 sputter cathodes which had a pure titanium target and a titanium carbide target respectively, and their compositionally gradient was realized by varying continuously the electric power supplied to each sputter cathode.

Under visual observation, the obtained Ti/C compositionally graded film appeared to be uniform and adhesive. According to AES in-depth profiles, the carbon (C) concentration in the film gradually decreased in depth direction from the surface toward the substrate, confirming that a Ti/C compositionally graded film had formed on the alloy substrate. On the basis of XRD, it was found that titanium carbide and α-titanium phases were formed in the gradient film, with TiC(200) and Ti(010) dominant respectively. Furthermore the Vickers hardness of the film reached over Hv=1800. Therefore the surface hardness of the alloy and the adhesion of the hard coatings were expected to be improved at the same time by this method.

REFERENCES

[1] S. G. Steinemann and S. M. Perren, *Titanium Sci. Technol.*, **2** , 1327-34 (1985).
[2] P. Galle, *Compt. rend.*, **299**, 535-39(1984).
[3] C. B. Johansson, J. Lausmaa, T. Roestlund and P. Thomson, *J. Mater. Sci. Mater. Med.*, **4**, 132-41 (1993).
[4] A. Montague, K. Merritt, S. Brown, J. Prayer, *J. Biomed. Mater. Res.*, **32**, 519-26 (1996).
[5] P. I. Branemark, U. Breine, R. Adell, B. O.Hansson, J. Lindstrom, A. Ohlsson, Scand. J. Plant. *Reconstr. Sur.*, **4**, 100-19 (1969).
[6] R. F. Bunshah, *Thin Solid Films*, **80**, 255-61 (1981).
[7] P.G.Th. van der Varst and G. de With, *Thin Solid Films*, **384**, 85-89 (2001).
[8] M. Jones, A. J. Horlock, P. H. Shipway, D. G. McCarthy and J. V. Wood, *Wear*, **251**, 1009-16 (2001).
[9] R. G. Radhakrishnan, R. E. Robertson, P. M. Adams and R. C. Cole, *Thin Solid Films*, **420**, 553-64 (2001).
[10] M. Numoto, *J. Surface Finishing Society of Japan*, **40**, 241-47 (1989).

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